BNWL-SA-5053
CONF-740727-2

METHANOL FROM FORESTRY, MUNICIPAL AND AGRICULTURAL ORGANIC RESIDUES

by

C. A. Rohrmann, L. K. Mudge, and V. L. Hammond
Pacific Northwest Laboratories

for the
1974 Engineering Foundation Conference
on
"Methanol Fuel"
July 7-12, 1974
New England College, Henniker, New Hampshire

July 1974

BATTELLE
Pacific Northwest Laboratories
RICHLAND, WASHINGTON 99352

EB

TABLE OF CONTENTS

Page No.

I. INTRODUCTION

II. CHARACTERISTICS OF REPRESENTATIVE AND SELECTED RESIDUES

III. PROCESSING

BNWL-SA-5053

METHANOL FROM FORESTRY, MUNICIPAL AND AGRICULTURAL ORGANIC RESIDUES

by

C. A. Rohrmann, L. K. Mudge and V. L. Hammond

I. INTRODUCTION

A. Objective

It is the objective of this paper to review the potentials for the use of renewable resources, specifically forestry, municipal and agricultural residues, as primary raw materials for the production of methanol. The basis for such processing would involve the conversion of the residues to a gaseous mixture of suitable composition such that methanol could be obtained by more-or-less conventional synthesis methods.

B. Methanol and Methanol Fuel

In the U.S. essentially all synthetic methanol (as distinct from the minor production of the so-called "natural" methanol recovered by the destructive distillation of wood) is produced from natural gas (methane). Prior to about 1950 substantial quantities were produced from the water gas obtained from coke. Up to the present time processes based on low-cost natural gas have completely replaced the original processes based on coke. The methanol produced from alternate materials such as the subject residues need not be purified to remove the higher alcohols or other organics. Such material is termed methanol fuel or methyl fuel. Essentially all of the synthetic methanol of commerce is the purified material and is used primarily for the production of other chemicals such as formaldehyde, monomers, esters, amines and solvents. For fuel uses it is likely that the catalytic processes used would be optimized to emphasize the formation of the higher alcohols to improve the fuel value of the product.

C. Technical Basis for Production of Methanol from Residues

The manufacture of methanol from residues is thus based entirely on the productive conversion of the carbon in such residues to carbon monoxide by partial oxidation with air or oxygen. The hydrogen content of the gaseous product would be increased to the desired level by employing the so-called shift reaction whereby a portion of the carbon monoxide would be made to react with water. Ideally these reactions would be made to proceed in a single step of the gasification process. In practice, however, a very complex series of reactions would take place. Also, to achieve optimum conversion, more than one reactor would probably be needed or multi-stage conditions would have to be provided in a single, more complicated, reactor.

Conceptually the raw residue with or without the addition of steam would be contacted at rather high (burning) temperature with air or oxygen. Under preferred conditions, tars and volatile organic matter would be essentially completely decomposed to yield a gas composed of carbon monoxide, carbon dioxide, hydrogen, water vapor and nitrogen (if air rather than oxygen is used as the oxidant). The following simple reactions (as well as more complex ones) would be expected to proceed:

$$(C_6H_{10}O_5)_x\text{(carbohydrates)} \rightarrow \text{Carbon} + H_2O$$

$$C + O_2 \rightarrow CO_2$$

$$C + 1/2\ O_2 \rightarrow CO$$

$$C + CO_2 \rightarrow 2CO$$

$$C + H_2O \rightarrow CO + H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

Many more complex reactions involving the decomposition of proteins, oils, fats and other organics would also certainly be taking place. However, the gasification process would in all cases be controlled to yield the most desirable composition of gases as indicated above plus a relatively small amount of inert residue or ash. The gas thus produced would be further processed to give the desired H_2:CO ratio by the shift conversion and to remove the carbon dioxide and residual oxygen along with particulate matter, excess water vapor and finally any contaminants such as hydrogen sulfide which would impair the performance or lifetime of the catalysts used in methanol synthesis.

By this means the principal organic matter in a wide variety of residues would be converted to a gas of rather simple composition and which would be made to be essentially the same as that required for any practical methanol production process. Or, in other words, the most important resource, carbon, in any of such residues is prepared for conversion to methanol and concurrently some of this same carbon is used to provide the necessary hydrogen by reaction with water. A great variety of presently wasted carbonaceous residues can thus be considered for use in methanol production. Furthermore, such wastes can be considered as major renewable resources of carbon.

D. Wastes or Residues as Renewable Resources of Carbon

Renewable resources of carbon would generally be regarded as comprising the wide variety of lost, wasted, dumped, burned or otherwise unproductively utilized vegetable matter such as lumbering residues, forest slash, wood waste, tree bark and other forestry industry wastes, paper and fiberboard trash, and garbage in municipal waste and the enormous volume of agricultural crop residues such as straw, stalks, leaves and stems plus the related food processing industry wastes such as seed hulls, fruit pits, nut shells and sugarcane bagasse. Details concerning the supply, location, composition and availability of many of these residues are not readily at hand. Furthermore, a similar situation exists for comprehensive data on the cost of gathering and delivery to a centralized point of use. Rather rough information on some of these residues are shown in Table I. The data for the lumber mill residues: sawdust, shavings, scrap and bark, are probably representative. Likewise, the data for municipal waste are probably representative. Agricultural residues, though very large in magnitude, are quite variable from year to year. Furthermore, the crops change and also involve some long-term trend changes. However, data for the major source of crop residues, corn and wheat, are probably constant and representative.

In Table II are listed all of the major farm crops with estimates as to the potential availability of residues from some of these. Because of excessive moisture content, animal manures are not included. However, in a comprehensive analysis, these should probably also be included. Similarly, the residues from the extensive food processing industry should be included.

E. Scale of Conversion Operations

On consideration of the data in Table I, it can be recognized that many of these residues in quantity are widely dispersed. The problem of economical

TABLE I. Certain Renewable (Waste) Carbon Resources (U.S.)

Source	Estimated Annual Quantity: Dry Basis Short Tons	Location	Approximate Carbon Content, wt%	Comment
Forestry (lumbering) Sawdust, shavings, bark and scrap	1.2×10^8	Total U.S. with 10^7 tons in the Pacific Northwest	50	As much as 10^6 tons already at individual locations
Municipal Residues: Trash and garbage	2.3×10^8	All metropolitan areas	46	Also reported as 0.825 ton per year per person
Agricultural Residues: Such as wheat straw and corn stalks	5×10^8	Midwest and Pacific Northwest	40	Principally field residues

TABLE II. The Major U.S. Farm Crops
(1968 Data, Rounded)

Crop	Tons	Estimated Residues Lbs Dry Matter/ Lb Product	Estimated Residues Tons
Corn	123,000,000	2.2	270,600,000
Wheat	47,000,000	2.3	108,200,000
Soybeans	31,000,000	1.2	37,200,000
Oats	15,000,000	1.6	24,000,000
Barley	10,000,000	1.5	15,000,000
Sugarcane	26,000,000 (Almost Half is Hawaiian)	---	---
Sorghum (Grain)	21,000,000	1.5	31,500,000
Rice	5,250,000	1.5	7,880,000
Cotton Seed	4,600,000	---	---
Grapes	3,600,000	---	---
Apples	2,700,000	---	---
Peaches	1,800,000	---	---
Peanuts	1,300,000	---	---
Tobacco	850,000	---	---
Sunflower (Seed)	750,000	1.6	1,200,000
Nuts (Walnuts, Almonds, Pecans)	240,000 (About Equal Amounts of Each)	---	---
		TOTAL TONS OF GRAIN RESIDUES	495,580,000
		CALL IT	500,000,000

Data are from Agricultural Statistics, USDA for 1968 and Yearbook of Agriculture, 1950-1951, Page 842 collection and delivery to the point of processing is thus the major one. Furthermore, to make a significant impact on the fuel energy scene, a large fraction of the major residues must be converted either in a number of modest-sized plants or a few very large plants serving a local area. In any case, it is reasonably clear that residues as reviewed in Table I represent an enormous resource of carbon. With production increases that have been realized since the data in Table II were obtained, it is conceivable that all of these combined carbon resources, including those of Table I, approximate that of the entire coal industry in the U.S. Recent coal production has been about 600,000,000 tons (70% carbon). The combined forestry, municipal and agricultural residues can be visualized as reaching about 1,000,000,000 tons (40% carbon). Thus the total of all these renewable resources when viewed on a carbon content basis is essentially equivalent to the annual U.S. production of coal. With some additional rather "broad brush" estimations such as a 50% conversion of the total carbon to methanol with a fuel value half that of gasoline, utilization of the total resource of these residues would yield liquid fuel equivalent to about 2,000,000,000 barrels of gasoline. Realism, of course, requires a much more modest assessment of this potential. However, if only one-fifth of this amount could be converted, this would amount to about a million barrels per day, which would be a significant contribution to the fuel supply. For isolated populations such as the Hawaiian Islands, an even greater contribution would appear to be possible with the conversion of all of their sugarcane bagasse to methanol rather than by dumping and inefficient burning, which are the present means of disposal.

The largest U.S. synthetic methanol plants in operation today produce over 200,000,000 gallons per year (or 700,000 tons per year). With residues containing 40% carbon and assuming a 50% conversion of this carbon to recovered methanol, this indicates the need for about 1,250,000 tons per year of residues to provide equivalent production. It is probable that in certain areas (but not generally) such quantities of forestry, municipal and agricultural residues could be provided. However, in order to make a significant impact on fuel supply, very many such facilities would have to be operated. Yet when the overall problems of waste disposal vs waste utilization and long-term fuel economics are considered, such use of renewable carbon resources may be haghly favorable.

II. CHARACTERISTICS OF REPRESENTATIVE AND SELECTED RESIDUES

A. General Basis

Except for rather minor industrial utilization of straw and bagasse for paper and the use of wood waste* and bagasse as fuel for boilers, no significant present utilization of residues for conversion to chemicals is known in the U.S. Thus it must be concluded at the start that no conversion processes are at hand today which can accept any of the residues. However, it is reasonable to expect that developments and facilities which are being prepared for gasification of coal (including synthesis gas production for methanol manufacture) should be suitable with minor modifications for the conversion of residues. Thus, although research and development may be needed to assure optimum conversion processes for residues, it is assumed that the basic process engineering being considered in the variety of coal gasification concepts can be satisfactorily applied for residue conversion. In Table III we are attempting to show the near-future value of carbon resources.

B. Characteristics and Preferences

1. Composition

Although considerable variation in composition (physical and chemical), especially in bulk municipal residues, can be expected, any conversion process requires a fair degree of physical uniformity, particularly, for example, in the means for charging material to a gasifier. Also from a process standpoint, massive and major concentrations of inert material must be removed. In addition, excessive moisture should be absent. Ideally, residues should therefore be reasonably dry, free of massive specimens of glass, metal or rock or high concentrations of dirt, in other words, predominantly combustible. Forestry and municipal residues would most likely need to be broken down to a manageable particle size by chipping or shredding. Agricultural residues may be most uniform in size and composition like sugar mill waste or bagasse are excessively wet, and may thus require

---

*And the use of wood waste for charcoal briquet manufacture.

TABLE III. Comparison of Representative Carbon Sources

Source	Wt% Carbon	Btu/lb	lbs/10^6 Btu	Delivered Prices			
				$/Common Unit	$/$10^6$ Btu	¢/lb	¢/lb C
Natural Gas (methane)	75	21,500	46.5	1.00/10^6 Btu	1.00	2.15	2.87
Fuel Oil (low sulfur)	85	19,130	52.35	11.00/BBL	1.84	3.52	4.14
Coal	70	12,000	85.00	13.00/ton	0.55	0.65	0.93
Residues*	40	6,500	154.00	8.00/ton**	0.62	0.40	1.00

* Forest, municipal or agricultural: dry basis, free of massive inerts such as glass, metal or rock.

** For some residues this is probably a high figure.

preliminary drying or blending with large amounts of low-moisture residues. Chemically there are some variations to be expected; however, all forestry, municipal and agricultural residues are mainly of plant or vegetable origin--cellulosic in nature--wood, bark, paper box board, straw, stalks, leaves and stems, etc. Plastics in municipal residue should tend to increase the carbon content. The carbon content of all such residues will be in the range of about 40 to 55% on a dry basis. Conservatively, it is considered for the purposes of this report, that available carbon for all such residues will average 40% by weight as delivered for processing.

In summary, the assumed likely and preferred composition of these residues may be about as follows:

Moisture	less than 20%
Inerts	less than 10% and free of massive specimens of metal, glass and rocks
Carbon	40%
Particle Size	Manageable and probably less than 5"

It should be recognized that these likely characteristics do not take into account what features may really be required by today's gasification equipment. Thus direct utilization is unlikely without equipment modifications. The details of such modifications have not yet been defined but will probably relate most particularly to particle size and moisture content.

2. Magnitude

Although many residues may be considered for conversion and some may have the most desirable characteristics, the consideration for their utilization for production of a large-scale energy source such as methanol may have to be dropped because the total quantity of such material is not sufficient to make a significant contribution to the total energy needs. The nut shells and the discarded pits from the fruit canning industry may be an example of this situation (peaches, apricots, olives, cherries and plums). However, there may be situations where a number of these different fruit-processing industries are concentrated and where the magnitude of their combined residues may be large enough to support a conversion process.

The major residue sources must therefore be given most attention. These include municipal residues, wastes from the intensified forestry industries and the residues from the largest agricultural crops such as corn and the small grains and sugarcane. Tree bark may be the most significant residue from the lumbering industry. For municipal residues the problem appears to be simply one of selecting a community of sufficient size and one with which the residue disposal problems are most acute.

3. Availability

By availability is meant not only the existence of an adequate quantity of residue but more importantly one that is accessible and readily accumulated, collected and delivered to the processing facility. The lumbering and municipal residues certainly provide the most favorable availability features, particularly if the processing facility can be provided near to or on the same property. The situation for most agricultural residues is generally not so favorable. But sugarcane bagasse is a most favorable example since, like forestry and municipal residues, collecting and delivery expenses have already been provided for. Although some bagasse is dumped, most is dewatered to the minimum extent necessary to assure its combustion as very low-grade fuel in a boiler. This is a disposal method with no credit taken for its fuel value. Any other means which can be justified economically is used, such as paper and fiberboard production. Similarly it would seem that utilization of its carbon content for other than fuel would also be favorable.

Although for some small grain crops a relatively small amount of the straw is collected for use, the threshing operation generally involves the discharge of a large fraction of the total straw which is grown. However, this discharge is generally by concurrent scattering back onto the field. Some machines do accumulate the straw and discharge it in massive piles from which subsequent collection can be easily done. It would seem that if the straw were to have only modest value, simple changes could be provided on threshing machines to provide for the accumulation and placement of large loads of straw for subsequent collection and hauling to the processing facility.

It is clear then that for utilization of the major agricultural residues, means must be assured for most economical accumulation, collecting and delivery. Bailing has been proposed and is used, but for lowest-cost delivery some other means are needed such as compaction or packing into extremely large bales (one ton or more). Such baling is already practiced with some newly-developed machinery for certain hay crops and may be suitable here.

In summary, the availability situation appears most favorable for forestry and municipal residues. Among agricultural residues, sugarcane bagasse also appears most favorable. For the other most likely agricultural residues, straw from the small grains and corn stalks are probably suitable but for widespread utilization more economical accumulation, collection and delivery systems need to be applied.

4. Reliability of Supply

For any of the major residues discussed above there do not seem to be any problems of assuring the reliability of the supply of residues to a processing facility. Because of trends toward more intensive attention to paper recycling, the composition of municipal residues may change somewhat over the years. In contrast the urban population is expected to continue to increase and the magnitude of the overall problem can be expected to intensify with more interest and need for productive utilization of such residues. Similarly in the forest industries there is a trend toward more complete utilization of the tree with a continued expansion of the industry with the net result expected to be a further increase in the supply of corresponding residues. Furthermore, if even a modest value for such carbon resources could be assured, it is very likely that larger quantities of material normally left in the woods would be retrieved and delivered.

Agricultural residues will probably continue to be at hand and also in higher yields per acre. This should favor a basis for a reliable supply. Furthermore, no significant shifts in major crop species are expected; corn and the small grains will continue to be grown where they are grown today and with greater yields.

5. Price

At this point it is not realistic to consider prices for residues; however, economics alone by the conventional views will not necessarily determine what happens to residues. For example, environmental, land use or aesthetic reasons may be overriding in determining what is to be done with them. This is certainly the probability with municipal garbage and trash but very likely very much less a probability for the forestry and agricultural residues. Except where burning is the usual practice, this is also being regarded as unacceptable.

If residues are viewed as carbon resources, which they are when considered in the energy picture, then consideration of their potential values (and price) appears reasonable. In Table III, it is clear that coal is by far the cheapest source of carbon. Furthermore, the U.S. has enormous coal resources. Thus the value of residues must be viewed with coal as a basis. Also the pricing of coal will probably change (increase) as other fuel (carbon) resources change (natural gas and oil) and as will the products made from them. For even the near future (the next ten years) a stable pricing situation for all of these carbon resources cannot be confidently anticipated. For the present moment, then, it would appear that residues on a carbon content basis would need to be priced at less than coal since coal is also being seriously considered as a methanol source as natural gas becomes less available and much more costly. In view of the data shown in Table III, residues that have zero value or very low costs for accumulation, collecting and delivery should probably receive primary attention for any conversion program.

In summary, then, a price or value on residues cannot be reasonably well established today; however, it is likely to be determined in relationship to coal, which is at present the cheapest carbon resource. Factors other than intrinsic value or price will determine the utilization of residues, particularly municipal residues.

C. Residues Most Likely to be Considered for Conversion

On the basis of composition, magnitude and assurance of supply, the residues most likely for consideration for conversion to methanol would be:

municipal residues, certain forest industry residues and bagasse as the agricultural residue. With economical means for accumulation, collection and delivery, straw from certain small grains, particularly wheat, should also receive major attention. The emphasis on these particular agricultural residues should not be taken as an indication that all others should be rejected. Some special situations could exist favoring consideration of others; however, a successful conversion program on straw could have the most far-reaching and overall beneficial impact on the energy situation because of the great magnitude of such residues including other grains and corn.

D. Characteristics of Selected Residues

Composition and properties of residues have been noted in a number of references with some inconsistencies and lack of precise identification of species and sources. The data in Table IV comprise a re-estimate from these various sources for the residues most likely to be considered.

III. PROCESSING

A. Processes for Gasification of Solid Fuels

Processes for the complete gasification of solid fuels are fairly well advanced and some have been used commercially for many years to generate gases from coal. Solid fuels include all solid combustible (carbonaceous) materials such as coal, lignite, wood, paper, agricultural and municipal residues and plastics. Up until recently efforts to improve the gasification technology have been mainly concentrated in the area of coal gasification. The technology developed may also be applied to many solid organic residues. Studies on refinements of the basic fuel processing schemes (gasification) are still in progress even though the technology for economic application of some gasification schemes is available.(1-5)

Basically, four different processing approaches have been considered for gasifying solid fuels: fixed bed, fluidized bed, entrained systems, and molten liquid suspension. Fixed bed gasifiers and entrained systems can be operated to extract dry ash (nonslagging) or molten ash (slagging). If the gasifier is oxygen blown, an intermediate (280-500 Btu/ft^3) Btu gas is obtained while air-blown gasifiers generate a low Btu gas (100-180 Btu/ft^3). Systems are operated at an atmospheric pressure or at elevated pressure.

TABLE IV. Composition of Representative Residues

% by Weight

	Municipal Residues,							
	As Received Dry Basis	Less Separable Inerts			Douglas Fir Bark (dry basis)	Hawaiian Bagasse (dry basis)	Wheat Straw
Paper	44.2	53.0	Carbon	44.4	56.2	46.2	40.0
Food Waste	16.6	20.0	Oxygen	42.0	36.7	45.9	42.0
Wood	2.5	2.9	Hydrogen	7.0	5.9	6.4	5.5
Textiles	2.3	2.7	Nitrogen	0.4	--	--	0.5
Leather, Rubber, Plastic	2.9	3.4	Moisture	12.3	--	--	7.0
			Sulfur	0.2	--	--	
Yard Waste (Organic)	5.0	6.0	Ash	5.9	1.3	1.5	5.0
			Btu/lb	6000	9570	7850	6500
Separable Inerts (glass, metal, rock)	16.5						
Dirt	10.0	12.0					

The following discussion of processes is presented in terms of the classification by method of fuel contact with reactant gases. Fixed bed, fluidized bed, entrained and molten liquid gasifiers are discussed in that order. Although the technology applies specifically to coal processing, application to solid organic residues is possible.

1. Fixed Bed

Fixed bed processes are characterized by a slowly-moving fuel bed supported by a grate. Fuel is added to the top of a vertical retort while ash is removed through the grate at the bottom. In usual operation for maximum thermal economy, the gaseous reactants are passed countercurrent to the direction of fuel flow, but units can be operated with cross-current and countercurrent flow.(6)

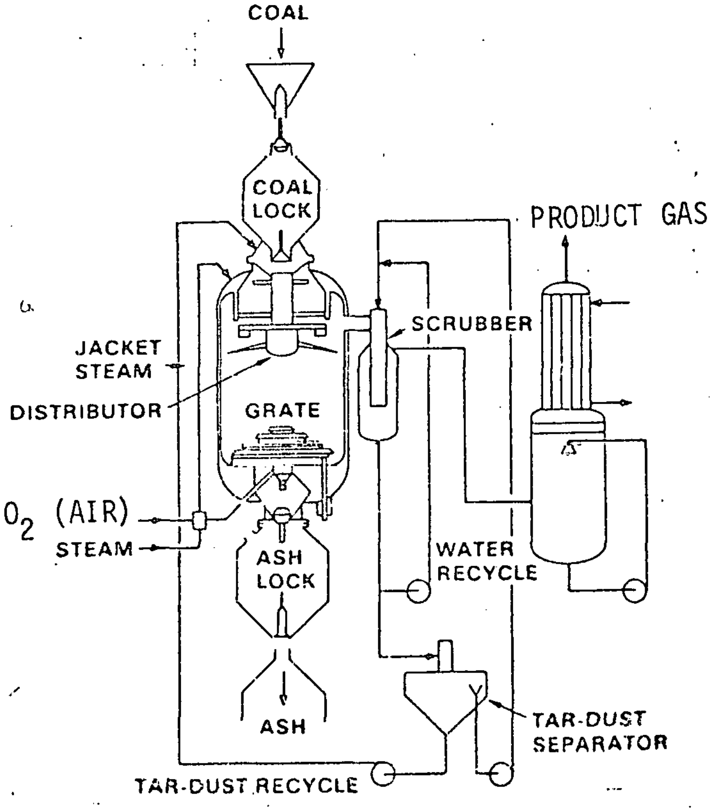
The linear flow rate of fuel through a fixed bed reactor is slow (0.7 to 2 ft/hr for coke);(7) the fuel residence time is correspondingly long. Reactant gas velocities based on the free cross section of the reactor are not over 3 ft/sec at operating conditions and are a function of the fuel size distribution.

Advantages of fixed-bed processes include high heat economy inherent in the counter flow of solid fuel and gasifying medium, high carbon conversion as a result of the long fuel residence time, and low solids content in the product gas. Disadvantages are also inherent in fixed-bed processes. Caking materials cannot be processed unless they are pretreated to render then noncaking, or unless the gasifier is modified mechanically to break up agglomerates.(8) Sized fuel must be used to attain maximum output. Production of tars in the upper, cooler zones of the fuel bed are troublesome and must be removed from the product gas. Specific processing rates are low in a fixed-bed gasifier, about 300 lb/hr ft^2 at 20 atm pressure for coal.(9)

A variety of fuels can be handled in a fixed bed gasifier. Properties of the fuel that are important in fixed bed gasifiers include the particle size distribution, caking tendency, ash fusion temperatures, and reactivity. Ideally the fuel should be noncaking, uniformly sized with few fines, and have a reasonably high mechanical strength. With this type of fuel, uniform gas distribution is obtained which results in stable reaction zones and uniform temperature distribution in the fixed bed. The ash fusion temperature establishes an upper temperature limit in non-slagging operations. The minimum practical temperature is determined by the reactivity of the fuel.

An example of a commercially-available, fixed-bed coal gasifier, the Lurgi gasifier, is given in Figure 1.(10) The Lurgi gasification system is classified as a high-pressure (300-500 psig), fixed bed, non-slagging, steam oxygen gasifier for producing gas from coal. The gasifier is a double-walled pressure vessel with the walls forming a water jacket for protection of the outer pressure vessel wall from high reaction temperatures. The jacket also furnishes some of the steam for the process. The inner wall confines the fuel bed where, by counter-current contact with oxygen and steam, the coal is gasified. Coal is fed into the gasifier through a lock hopper system where it is distributed by a rotating arm. Oxygen and steam are introduced into the fuel bed through the rotary grate at the bottom. The coal charge travels downward in the gasifier where it is dried, devolatilized and gasified. The resulting ash is removed by the rotating grate through an ash lock on the bottom of the gasifier.

FIGURE 1. Lurgi Gasifier(10)



The hot crude gas leaving the gasifier contains steam, tar, oil, naptha vapors, other hydrocarbons and sulfur compounds and is scrubbed in a washer-cooler with circulating gas liquor to reduce its temperature. The partially-cooled gas, saturated with steam, passes to a waste heat boiler. The cooling helps to condense heavy tar fractions and gas liquor at this time. The crude gas leaving the waste heat boiler is further processed for synthesis gas for fuel and chemicals or town gas. The thermal efficiency of the Lurgi gasifier is between 85 and 90 percent. The Lurgi process has been used commercially since 1936, so that the process is proven, although it does have certain operating limitations characteristic of fixed bed gasifiers.

2. Fluidized Bed

Fluidized bed gasifiers are an intermediate between the fixed bed and entrained suspension gasifiers. The gas velocity in the fluidized bed is increased to the point where the pressure drop in the bed is sufficient to lift the particles. At this point, the bed expands and the individual fuel particles are no longer in continuous contact. In this way the bed of solids is imparted random motion properties similar to a fluid. Gas and fuel are contacted in a countercurrent fashion in fluidized bed reactors. Slagging operation is not possible.

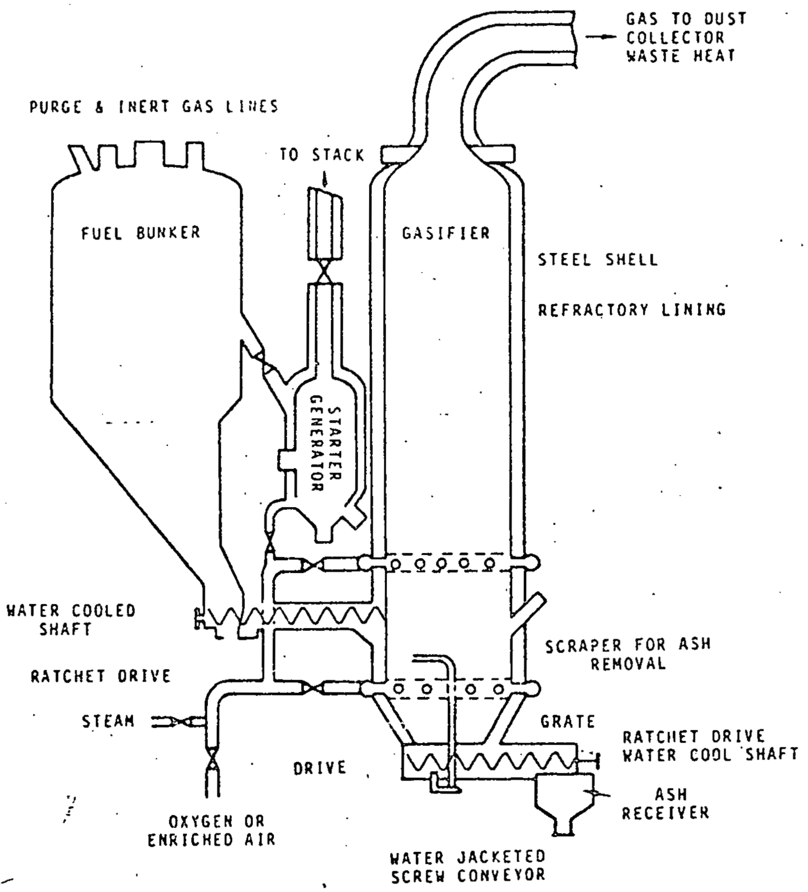
In general, fluidized bed processes can accept fuels with wide variations in quality--high ash and sizes from 0 to 8mm. Specific gasification rates are higher than with fixed bed units, which reduce the ground area required for a given plant size. The high fuel inventory in a fluidized bed gasifier minimizes the chance of oxygen breakthrough and, therefore, gives a high degree of reliability and safety. A fluidized bed system can be operated over a wide range of output without a significant loss in efficiency. Excellent heat transfer and particle mobility in a fluidized bed prevents local overheating which can result in clinker formation. Disadvantages in operating a fluidized bed process include the following: (1) high sensible heat loss in the product gas as a result of the uniform temperature in the fluidized bed; some of this heat can be recovered in waste heat boilers but is not available for fuel gasification as in a fixed bed process. (2) Carbon carryover in the product gas can result in high fuel losses, particularly with unreactive or friable fuels. (3) A large, steady-state ash content is required in the fluidized bed to attain complete carbon conversion since intimate mixing is characteristic of fluidized beds. (4) The range of possible operating conditions is restricted by the fluidization characteristics of the fuel.

Fluidized beds for gasification of coal have been used on a commercial scale in the Winkler process since the 1920's. The Winkler process is a fluidized bed, atmospheric pressure system for the production of synthesis gas from coal. The generator is a cylindrical, refractory-lined vessel, 13 to 15 ft in diameter and 65 ft high. Coal feed is usually crushed to 0-3/8 in. and dried, although moisture contents in coal of over 8 percent can be tolerated. Coal is fed to the Winkler generator through variable speed screws which serve as seals to prevent back flow of gases. The gasifying medium fluidizes the coal bed and gasifies the coal at a uniform temperature. Oxygen (or air)-steam mixtures are added at the bottom and top of the bed. Top addition is used to increase the carbon conversion in the gasifier. Care must be taken in the top addition since too little oxygen-steam will result in high carbon losses and too much will burn synthesis gas unnecessarily. The highest temperatures in the Winkler system occur at the top of the fluid bed. A schematic of a Winkler gasification process is shown in Figure 2.(11) Of over 30 Winkler generators that have been built, six are presently operating, two in Kutahya, Turkey, three in Madras, India, and one in Gorazde, Yugosalvia.

3. Entrained Suspension

In the entrained suspension system, fuel is carried fully entrained in the gasifying medium. The ability of the entrained suspension system to handle any type of fuel is the most important characteristic of the process that has prompted considerable interest. The fuel is pulverized and during operation of the gasifier the individual fuel particles are separated and discreet which makes the caking properties unimportant in the operation of the process. Similarly, the ash fusion temperature is not important except in determining conditions for slagging and non-slagging operation. An inherent characteristic of entrained suspension

FIGURE 2. Winkler Gasifier(11)



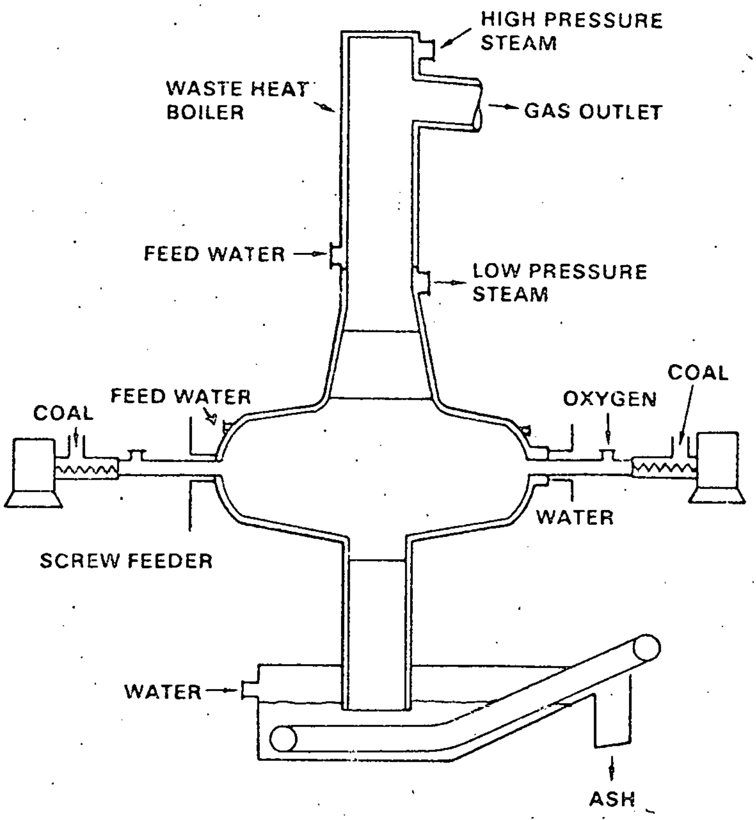
is the production of a synthesis or producer gas that is free of tars and has very little methane. Certain limitations in entrained gasification result from the low concentration of fuel in the system and from the concurrent flow of fuel and gasifying medium. Carbon carryover is usually high. Fuel conversions are usually limited to 85 to 90 percent for economic reasons. Char carryover can be separated from the product gas with cyclone collectors and recycled to the gasifier to improve the fuel conversion. With concurrent flow, the temperature of the product gas is high (2700°F in the Koppers-Totzek gasifier) which necessitates heat recovery from the gases to achieve good process thermal efficiency. Heat recovery is complicated by the presence of solids, and in some cases, molten ash particles which must not be allowed to contact heat transfer surfaces. In spite of these disadvantages, the overall energy production rate per unit volume of reactor is greater under similar slagging or nonslagging conditions than in fluidized bed or fixed bed systems. The adverse effect of low fuel inventory is more than offset by the large surface area of the pulverized coal particles.

The Koppers-Totzek gasifier, shown schematically in Figure 3, is an oxygen blown, atmospheric pressure, entrained suspension system used extensively for H_2 production for ammonia synthesis. Over 50 gasifiers of this type have been built, 20 in the last four years. Pulverized coal, 90 percent under 200 mesh, is screw fed from hoppers into pairs of burners situated opposite each other on the same axis so that their jet discharges converge. A gasifier may contain two or four such burner heads. Oxygen conveys the coal from the screw feeders to the burner nozzles at velocities sufficient to prevent flame propagation into the feeder tubes (300 ft/sec). Coal is dried to about 1 weight percent moisture, but moisture contents of 4 to 8 weight percent can be tolerated. The gasifier is refractory lined with a water jacket where process steam is raised. Sufficient steam is added to the burner nozzles to maintain the flame temperature at about 3500°F. Gas temperature at the reactor exit is about 2700°F. About 50 percent of the coal ash leaves at the bottom of the reactor as a slag which is quenched and granulated in water. The remainder leaves as fly ash with the product gas and is removed in gas cleanup. Waste heat boilers are used to recover the sensible heat in the high-temperature product gases. The gas is further cooled and cleaned in conventional, commercially-proven processes.(12)

4. Molten Bath

In molten bath systems for gasification of solid fuels, the fuel is devolatilized by contact with the hot liquid and gasified by gases purging through the liquid suspension. Molten salts and molten iron have been studied for this application. No molten bath system for fuel gasification has been commercially demonstrated. The MW Kellogg Company has doing considerable work on a process based on the use of fused alkali metal carbonates.(13) The feasibility of using molten salt for the processing of municipal wastes has been investigated in an EPA study.(14)

FIGURE 3. Koppers-Totzek Gasifier(11)



Advantages of molten bath systems include: (1) the ability to handle all types of solid fuels, (2) high gas yields as a result of the catalytic effect of the molten media, and (3) production of a gas free of tars and low in particulates. The corrosive nature of the molten media and the complicated ash removal are the major drawbacks to this type of system.

B. Application to Selected Residues

Probably any of the processes for gasification of solid fuels which were discussed in the previous section could be used for generation of synthesis gas from organic residues. Characteristics of organic residues that are important when considering their processing in conventional equipment are discussed in the following paragraphs.

A fixed bed reactor, such as the Lurgi, requires a noncaking, closely-sized feed material for efficient operation. The presence of fines in the feed can cause channeling and can seriously impair the processing rates that can be obtained. Likewise, channeling may occur if attempts are made to process feed materials that melt and thus agglomerate. Generally, organic residues such as forest wastes, straw, and municipal refuse make a suitable feed to a fixed bed reactor since they are noncaking and can be shredded or chopped without the generation of a high percentage of fines. Municipal refuse and wood wastes have been gasified in a fixed bed reactor at Battelle-Northwest. Moisture contents up to 45 percent in the refuse feed can be tolerated in the process. The composition of typical municipal refuse is shown in Table V. Compositions of the gas obtained are presented later on.

TABLE V. Analysis of Municipal Refuse

Ultimate Analysis	% by Weight
Moisture	5.08
Carbon	45.91
Hydrogen	7.06
Oxygen	28.82
Nitrogen	4.19
Sulfur	0.10
Chlorine	0.32
Ash	14.18
Proximate Analysis	
Moisture	5.08
Volatile at 950°C	80.74
Ash	14.18
Btu/lb	7203

Use of entrained suspension and fluidized bed reactors for gasification of organic residues is possible but would require considerable pretreatment of the feed material. For example, the feed size for an entrained suspension system for coal is generally 80 percent minus 200 mesh which requires shredding and pulverizing of the feed. In order to assure an acceptable conversion, the residue must be predried to less than 8 percent moisture for fluidized bed and entrained suspension systems. Entrained suspension systems have the advantage of no tar products. Throughput rates are higher than for fixed bed reactors.

Molten salts for processing of organic residues have a number of advantages: 1) processing rates are high; 2) any feed size distribution can be tolerated; and 3) complete conversion to a gaseous product with no tars can be obtained. The major limitations of molten salt systems are the materials for containment and for handling of molten salt and ash removal from molten salt. Gas compositions obtained while processing municipal refuse in molten Na_2CO_3 are presented in the following section.

In general, the heating value of renewable resources is low (generally about 6500 Btu/lb)* which means that the conversion process must be efficient and require a minimum number of feed handling operations. Therefore, processes that require extensive preconditioning (pulverizing, grinding and drying) of the feed are not preferred. The disadvantage of extensive feed conditioning must, however, be weighed against possible advantages the process may have, such as a high quality synthesis gas that requires a minimum of shift conversion and cleanup. For most renewable resources, a fixed bed reactor can be employed for generation of synthesis gas.

Gasification of renewable resources with an O_2-steam mixture would yield a synthesis gas, or an intermediate Btu gas, that does not have the N_2 content of the gases shown in Table VI and should be suitable for conditioning to produce methanol. It should be emphasized that the compositions of gas shown in Table VI are for a specific set of operating parameters, and variation of such things as the steam content in the air blast and the air-steam preheat temperature influences the gas composition. Similarly, parameters for operation with an oxygen-steam mixture could be adjusted to give the desired gas composition for methanol synthesis.

---

*However, it should be emphasized that this low-heating value is essentially the same as that for lignites which are being intensively studied for conversion to gas of high Btu content (SNG).

TABLE VI. Pyrolysis Gas Compositions from Renewable Resources (Battelle-Northwest Gasifier)

	Volume %								Gross Heating Value Btu/ft^3
Resource	H_2	CH_4	C_2H_6	C_2H_4	CO	CO_2	N_2	O_2	
Wood Waste	20.6	2.1	0.2	0.1	24.1	13.4	38.9	>0.02	179
Municipal Refuse	20.3	1.3	1.2	0.7	9	15.5	52.0	>0.02	147

C. Resulting Synthesis Gas Characteristics

Synthesis gas for conversion to methanol in a conventional plant could be produced from renewable resources by gasification or pyrolysis. Some experience on gasification of wood wastes and municipal refuse with an air-steam mixture in a fixed bed reactor has also been gained at Battelle-Northwest. Sample compositions on a dry basis of the gas obtained are shown in Table VI. The ultimate and proximate analysis of the municipal refuse used in the process was shown in Table V.

Conversion efficiency on an energy basis for the production of the low-Btu gas shown in Table VI was about 85%. Tar production was observed but was not a significant portion of the weight of the residue (less than 1%). A significant quantity of aqueous phase condensate containing about 20 wt% organics was noted but the yield was not accurately determined since the product gas mixture was consumed in a secondary burner without cooling and condensing the aqueous phase.

Molten salt (Na_2CO_3) pyrolysis at 900°C of municipal refuse on a laboratory scale with the analysis shown in Table VI yielded a gas product of the composition shown in Table VII. The gas was forced to bubble through the molten salt before flowing from the pyrolysis reactor. Yield of gas was 65% of the weight of the refuse feed. The gas obtained by simple pyrolysis, as shown in Table VII, in a molten salt would make a suitable methanol synthesis gas.

TABLE VII. Composition of Molten Salt Pyrolysis Gas

Component	Volume %
H_2	40.6
CO_2	11.9
C_2H_4	1.8
C_2H_6	0.2
CH_4	11.6
CO	33.9

D. Synthesis Gas Conditioning

Composition of a synthesis gas such as shown in Table VII could be adjusted to give the desired H_2-CO mixture by reforming and shift conversion. The main reactions that occur are the following for reforming:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2$$

and for shift conversion:

$$CO + H_2O \rightleftarrows CO_2 + H$$

The last reaction is used for adjustment of the H_2:CO ratio for synthesis of methanol by the following reaction:

$$2H_2 + CO \rightarrow CH_3OH$$

Commercial processes are available for shift conversion and for removal of CO_2 and impurities from the synthesis gas. The composition of gases produced at Battelle-Northwest from wood wastes and municipal residues were as shown in Table VI.

D. Collection and Transportation Costs

The costs associated with getting wastes from the point of production to a central processing plant may be the only costs involved in obtaining the resources and would include collection, intermediate storage, transfer, hauling and final storage costs. Typical costs for performing some of these functions for municipal, agricultural and wood wastes are shown in Table VIII. When these wastes have no value and must be disposed of, the generator of them has to pay these costs plus the cost of final disposal. The total cost of

TABLE VIII. Estimated Collection and Transportation Costs for Municipal, Agricultural and Wood Wastes

Cost Item	Municipal Waste	Agricultural & Wood Waste
Collection Cost, $/ton	$12.50	$4.00
Transfer Station Costs, $/ton	2.50	2.00
Transportation Costs, $/ton mile		
Compactor Trucks	0.20	--
Diesel Tractor Trailer	0.06	0.06
Landfill Cost, $/ton	1.50	--

performing all these functions can range from $2 to $50 per ton of waste depending on the magnitude of parameters that are associated with the cost of collection and disposal of wastes.

It is difficult to establish a general case to determine if it is economically feasible to convert waste to a methanol fuel. For this review, we will discuss one case for municipal waste and one for agricultural or wood waste.

The cost of disposing of municipal waste in the United States today includes, at a minimum, the cost of collection and the cost of disposal by landfill to meet the minimum environmental standards. For a typical city in the United States today, the costs would be about $12.50 for collection and $1.50 for landfill operations. If no land were available within a reasonable distance of the city, transfer station and hauling costs would have to be added. For an equivalent cost to the generator of this waste, the waste could be moved to a central transfer station for loading into large tractor trailers for transportation to a methanol fuel production plant. In order to keep the cost the same to the producer of the waste as for minimum disposal requirements, the delivered price of the waste could include no more than $1.00 of the cost for the operation of the transfer situation. If the allowable value for the waste as a feedstock to a methanol fuel production plant is $8.00 per ton and this amount was credited to the generator of the waste, then $7.00 would be available for hauling the waste to the processing plant. With an allowance of $0.06 per ton/mile for the cost of transportation, this analysis shows that waste can thus be transported up to 115 miles to a processing plant at no additional charge to the generator of waste over the least costly disposal method (hauling to a land fill).

In most instances in the United States today, agricultural and wood wastes are presently burned on the land where they are generated. The burning of grass, straw and other vegetable matter such as tree slashings is soon to be outlawed in the state of Oregon, and other states are sure to follow this practice to reduce air pollution. For the present, the delivered price of sgricultural and wood wastes must include all the cost of collection, storage and hauling if these wastes are to be used for the production of methanol fuel. Based on present costs for harvesting and hauling of agricultural products, it is estimated that agricultural wastes could be collected, stored and transported up to 33 miles to a processing plant and still stay at about $8.00/ton. As environmental regulations become more stringent, the options to the generators of these wastes will become more limited and they will have to bear a higher disposal cost which will, in turn, allow wastes to be hauled a longer distance to processing plants and still be economical at the net delivered price of $8.00 per ton of waste.

E. Co-Product Possibilities, Fixed Nitrogen

In the operation of any carbon conversion process to yield synthesis gas for methanol production, considerable effort will be applied to achieve effective reaction between water and carbon monoxide to yield suitably high ratios of hydrogen to carbon monoxide in the synthesis gas stream. Thus carbon should always be considered as an effective material to produce hydrogen from water. Furthermore, that portion of the carbon involved in this hydrogen production reaction generally would be discarded as useless carbon dioxide from one of the gas purification steps. With the major carbon resources which exist in certain residues, production of more hydrogen than is necessary for methanol manufacture may be achieved. With the use of air or air-oxygen blends in the gasification process, it is conceivable that a synthesis gas composition could be obtained which could be used in an integrated process to yield directly both methanol and anhydrous ammonia. It may be recalled by some that just such a combination of processes was used by du Pont in the first U.S. synthetic ammonia production plant at Belle, West Virginia in 1927. In that process the air-coke-water reactions were used to produce the hydrogen for ammonia manufacture. A methanol production step was included in the head end to remove the residual carbon monoxide from the ammonia synthesis gas. A similar combination of processes would seem to be practical for the conversion of residues. In addition, circumstances may encourage further processing of the ammonia to urea whereby a more productive use could be made of the carbon from the residues by employing the otherwise wasted carbon dioxide and nitrogen which evolve from the earlier hydrogen production reactions. For purposes of review, the following simplified reactions would be involved:

Residue Gasification	Carbon + Oxygen (air) + $H_2O \rightarrow CO + N_2 + H_2$
"Shift" Reaction for Hydrogen Production	$CO + H_2O \rightarrow CO_2 + H_2$
Methanol Synthesis	$CO + 2H_2 \rightarrow H_3COH$
Ammonia Synthesis	$N_2 + 3H_2 \rightarrow 2NH_3$
Urea Synthesis	$2NH_3 + CO_2 \rightarrow (NH_2)_2\ CO + H_2O$

Although fixed nitrogen production is not the subject of this conference, it could be involved as it has in the past with methanol manufacture. Such an integration may result in some significant benefits both to methanol production as well as more efficient utilization of residues (carbon) and assurance of a supply of liquid fuel and essential fertilizer to the intensified U.S. agriculture industry.

REFERENCES

1. Schora, F. C., Jr., "Studies of Coal Gasification," paper presented at the Synthetic Fuels from Coal Conference, University of Oklahoma, Stillwater, Oklahoma, May 3, 1971.

2. Goldberger, W. M., "The Union Carbide Coal Gasification Process - Status of the Development Program," presented at Fourth Synthetic Pipeline Gas Symposium, Chicago, October 30-31, 1972.

3. Robson, F. L., et al., "Technological and Economic Feasibility of Advanced Power Cycles and Methods of Producing Nonpolluting Fuels for Utility Power Station," PB 198 392, December 1970.

4. Wen, C. Y., Optimization of Coal Gasification Processes, R&D Report No. 66, Interim Report No. 1, v. 1, Chapters I-VIII, West Virginia University, Morgantown, West Virginia, 1972.

5. Linden, H. R., "A Reassessment of the Prospects for Coal Gasification," Coal Age, pp. 73-79, May 1971.

6. Shirer, G. C., Chemical Engineering Mining Review, pp. 43-50, August 15, 1958; pp. 41-47, May 1971.

7. Gumz, W., Gas Producers and Blast Furnaces, John Wiley & Sons, Inc., New York, p. 70, 1950.

8. Lewis, P. S., Liberatore, A. J., and McGee, J. P., "Strongly Caking Coals Gasified in a Stirred-Bed Producer," RI 7644, Bureau of Mines, Morgantown, West Virginia, 1972.

9. Hottel, H. C., and Howard, J. B., New England Technology - Some Facts and Assessments, The MIT Press, Cambridge, Massachusetts, and London, England, 1971.

10. "Power Plant Integrated with Pressure Gasification of Coal," Combustion, v. 42, No. 8, 1970-1971).

11. Kasturiranzan, V. N., Satyapal, M., Iyer, R. R., Rao, D. G., and Chatterji, S. B., Indian Government Sponsored Study of Commercial Coal Gasification Processes - Koppers-Totzek, Lurgi and Winkler, reproduced by the Koppers Company, Inc., Pittsburgh, 1973.

12. Farnsworth, J. F., Leonard, H. F., Mitsak, D. M., and Wintrell, R., "Production of Gas from Coal by the Koppers-Totzek Process," paper presented at Clean Fuels from Coal Symposium, Institute of Gas Technology, Chicago, 1973.

13. MW Kellogg Company, "Commercial Potential for the Kellogg Coal Gasification Process," Research and Development Report No. 38, prepared for the Office of Coal Research, 1968.

References (cont'd)

14. Battelle-Northwest Final Report, "Feasibility Study of Use of Molten Salt Technology for Pyrolysis of Solid Waste," for National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio, April 1974.